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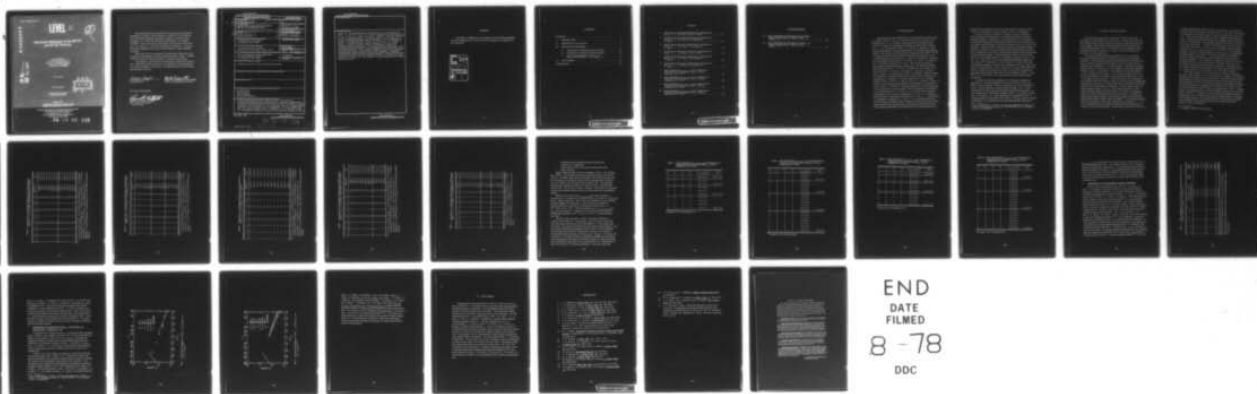
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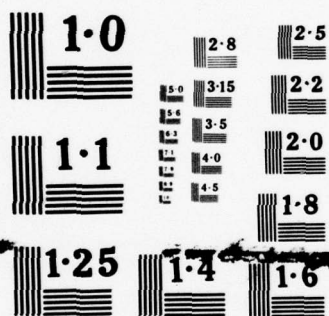
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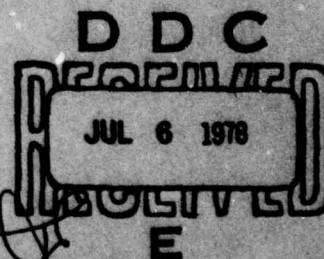
Vibrational Relaxation in the HF-DF and DF-HF Systems

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8 June 1978

Interim Report

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AIR FORCE WEAPONS LABORATORY
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This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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number v_1 . The computed rate coefficients for the $v \rightarrow v$ processes were $k(v_1 = 1, v_2 = 0; v'_1 = 0, v'_2 = 1) = 1.6 \times 10^{12} \text{ cm}^3/(\text{mole-sec})$ and $k(v_1, v_2 = 0; v'_1 = v_1 - 1, v'_2 = 1) = 1.4(v_1 - 1) k(1, 0; 0, 1)$ at 300 K. The rate coefficients for the $v \rightarrow v$ processes $\text{HF}(v_1 = 1) + \text{DF}(v_2) \rightarrow \text{HF}(v'_1 = 0) + \text{DF}(v'_2 = v_2 + 1)$ with $v_2 = 1$ through 3 decrease with increasing v_2 . The rate coefficients for the $v \rightarrow v$ processes $\text{HF}(v_1) + \text{DF}(v_2 = 1) \rightarrow \text{HF}(v'_1 = v_1 - 1) + \text{DF}(v'_2 = 2)$ with $v_1 = 1$ through 3 decrease with increasing v_1 . The $v \rightarrow R$ energy-transfer processes for $\text{HF}(v_1) + \text{DF}(v_2 = 0)$ and $\text{DF}(v_1) + \text{HF}(v_2 = 0)$ collisions occur by nonresonant $v \rightarrow R$ intramolecular energy transfer. The vibrationally excited molecule converts multiquanta of its vibrational energy into rotational energy. This process provides a mechanism for populating extremely high rotational states of HF and DF molecules. A rotational nonequilibrium model is used to calculate temperature-dependent quenching rate coefficients for vibrational relaxation of $\text{HF}(v_1 = 1)$ by $\text{DF}(v_2 = 0)$ and of $\text{DF}(v_1 = 1) + \text{HF}(v_2 = 0)$. The results are in good agreement with available experimental data.

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PREFACE

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CONTENTS

PREFACE	1
I. INTRODUCTION	7
II. METHOD OF CALCULATION	9
III. RESULTS AND DISCUSSION	11
A. Vibrational-to-Rotational Energy Transfer	11
B. Vibrational-to-Vibrational Energy Transfer	23
C. Vibrational Relaxation of HF($v_1 = 1$) by DF($v_2 = 0$) and of DF($v_1 = 1$) by HF($v_2 = 0$)	27
IV. CONCLUSIONS	31
REFERENCES	33

TABLES

1.	Vibrational-to-Rotational Detailed Rate Coefficients for HF($v_1 = 1, J_1 = 2$) + DF($v_2 = 0$) at $T = 300$ K	12
2.	Vibrational-to-Rotational Detailed Rate Coefficients for HF($v_1 = 2, J_1 = 2$) + DF($v_2 = 0$) Collisions at $T = 300$ K	13
3.	Vibrational-to-Rotational Detailed Rate Coefficients for HF($v_1 = 3, J_1 = 2$) + DF($v_2 = 0$) Collisions at $T = 300$ K	14
4.	Vibrational-to-Rotational Detailed Rate Coefficients for DF($v_1 = 1, J_1 = 3$) + HF($v_2 = 0$) at $T = 300$ K	15
5.	Vibrational-to-Rotational Detailed Rate Coefficients for DF($v_1 = 2, J_1 = 3$) + HF($v_2 = 0$) Collisions at $T = 300$ K	16
6.	Vibrational-to-Rotational Detailed Rate Coefficients for DF($v_1 = 3, J_1 = 3$) + HF($v_2 = 0$) Collisions at $T = 300$ K	17
7.	Rate Coefficients $k_{v_1, v_2; v'_1, v'_2}$ for Vibrational-to- Rotational Energy Transfer in HF(v_1) + DF(v_2) Collisions at $T = 300$ K	19
8.	Rate Coefficients $k_{v_1, v_2; v'_1, v'_2}$ for Vibrational-to- Rotational Energy Transfer in DF(v_1) + HF(v_2) Collisions at $T = 300$ K	20
9.	Rate Coefficients $k_{v_1, v_2; v'_1, v'_2}$ for Vibrational-to- Rotational Energy Transfer in DF(v_1) + HF(v_2) Collisions at $T = 300$ K	21
10.	Rate Coefficients $k_{v_1, v_2; v'_1, v'_2}$ for Vibrational-to- Rotational Energy Transfer in DF(v_1) + HF(v_2) Collisions at $T = 300$ K	22

TABLES (Continued)

11.	Rate Coefficients for Vibrational-to-Vibrational Energy Transfer $\text{HF}(v_1) + \text{DF}(v_2) \rightarrow \text{HF}(v_1 - 1)$ $+ \text{DF}(v_2 + 1)$	24
12.	Rate Coefficients for Vibrational-to-Vibrational Energy Transfer $\text{DF}(v_1) + \text{HF}(v_2) \rightarrow \text{DF}(v_1 + 1)$ $+ \text{HF}(v_2 - 1)$	25

I. INTRODUCTION

Measurements of rate coefficients for energy transfer and deactivation processes in $\text{HF}(v_1) + \text{DF}(v_2 = 0)$ collisions have not been reported in the literature for $v_1 > 1$. The laser-excited fluorescence method has been used¹⁻⁶ to measure the temperature-dependent quenching rate coefficient for $(v \rightarrow v + v \rightarrow R)$ processes in $\text{HF}(v_1 = 1) + \text{DF}(v_2 = 0)$ collisions. These measurements indicate rapid coupling between the vibrational and rotational motions. The laser-excited fluorescence technique has been used^{1,4,6} also to measure the temperature-dependent quenching rate coefficient for the $v \rightarrow R$ deactivation process in $\text{DF}(v_1 = 1) + \text{HF}(v_2 = 0)$ collisions. Because of the large endothermicity (1055 cm^{-1}) in $\text{DF}(v_1 = 1) + \text{HF}(v_2 = 0)$ collisions, the $v \rightarrow v$ process is assumed not to occur. This has been confirmed in laser-excited induced fluorescence experiments. The double exponential decay observed in $\text{HF}(v_1 = 1) + \text{DF}(v_2 = 0)$ collisions, for example, is not observed in $\text{DF}(v_1 = 1) + \text{HF}(v_2 = 0)$ collisions. The upper v_1 levels in $\text{DF}(v_1) + \text{HF}(v_2 = 0)$ collisions also reflect $v \rightarrow R$ transfer. These processes are endothermic, and the endothermicity increases with increasing v_1 for single quantum v transitions. We assume that the role of $v \rightarrow R$ energy transfer in $\text{HF}(v_1) + \text{HF}(v_2 = 0)$, $\text{HF}(v_1) + \text{DF}(v_2 = 0)$, and $\text{DF}(v_1) + \text{DF}(v_2 = 0)$ collisions can be deduced experimentally from studying $v \rightarrow R$ processes in $\text{DF}(v_1) + \text{HF}(v_2 = 0)$ collisions. Flow-tube studies have been carried out at room temperature by Airey and Smith,⁷ Kwok and Wilkins,⁸ and Smith⁹ on $v \rightarrow R$ relaxation of $\text{DF}(v_1 \geq 1) + \text{HF}(v_2 = 0)$. Airey and Smith⁷ reported a 36% increase in the $v \rightarrow R$ rate in going from $v_1 = 1$ to $v_1 = 2$. Kwok and Wilkins⁸ found a v^2 dependence in going from $v_1 = 1$ to $v_1 = 3$. Smith⁹ found a v dependence in going from $v_1 = 1$ to $v_1 = 5$. These discrepancies and lack of accurate rate data for upper vibrational levels point out the need for further experimental measurements and theoretical calculations of both v and temperature-dependent rate coefficients for the energy-transfer and

deactivation processes that occur from upper vibrational levels in $\text{HF}(v_1) + \text{DF}(v_2 = 0)$ collisions as well as in $\text{DF}(v_1) + \text{HF}(v_2 = 0)$ collisions.

Previous trajectory studies^{10,11} on $\text{HF}(v_1) + \text{HF}(v_2)$ and $\text{DF}(v_1) + \text{DF}(v_2)$ collisions predicted the role of rotational degrees of freedom in reaction dynamics. In particular, it was found that one or more quanta of vibrational energy of the vibrationally excited HF or DF molecule is converted into rotational energy of the same molecule in $\text{HF} + \text{HF}$, and $\text{DF} + \text{DF}$ collisions. This conversion of vibrational energy into rotational energy of the same molecule occurs by an intramolecular energy-transfer process and is responsible for formation of high rotational states of hydrogen halides and their isotopic analogs. Such high rotational states cannot be formed from chemical pumping reactions, for example, such as $\text{H} + \text{F}_2$ or $\text{F} + \text{H}_2$. The $v \rightarrow v$, $v \rightarrow R$, and $R \rightarrow (R', T)$ rate coefficients presented in these previous studies^{10,11} provide the rate data required to calculate both v and temperature-dependent quenching rate coefficients for $\text{HF}(v_1) + \text{HF}(v_2)$, and $\text{DF}(v_1) + \text{DF}(v_2)$ systems. The $v \rightarrow R$ and $R \rightarrow (R', T)$ rate coefficients were used in a rotational nonequilibrium model* to evaluate the temperature-dependent quenching rate coefficients for self-relaxation of $\text{HF}(v_1 = 1)$ and $\text{DF}(v_1 = 1)$. The results were in good agreement with available experimental data.

A trajectory study was undertaken to calculate the temperature-dependent $v \rightarrow R$ rate coefficients that occur in the $\text{HF}(v_1) + \text{DF}(v_2)$ and $\text{DF}(v_1) + \text{HF}(v_2)$ systems. This work completes our trajectory studies of $\text{HF}(v_1) + \text{HF}(v_2)$ collisions and their isotopic analogs. The $v \rightarrow R$ rate coefficients are used to calculate temperature-dependent quenching $v \rightarrow R$ rate coefficients for vibrational relaxation of $\text{HF}(v_1 = 1)$ by $\text{DF}(v_2 = 0)$ and $\text{DF}(v_1 = 1)$ by $\text{HF}(v_2 = 0)$. Rate coefficients are calculated for 12($v \rightarrow v$) energy-transfer processes that occur in $\text{HF}(v_1) + \text{DF}(v_2)$ collisions. Eleven of the twelve $v \rightarrow v$ processes have not been experimentally determined.

*R. L. Wilkins and M. A. Kwok, "Temperature Dependence of $\text{HF}(v_1 = 1) + \text{HF}(v_2 = 0)$ Vibrational Relaxation," TR-0078(3603)-5, The Aerospace Corp., to be published.

II. METHOD OF CALCULATION

The potential energy surface used here for HF-DF and DF-HF interactions is constructed from two functions, a London-Eyring-Polanyi-Sato (LEPS) potential energy function for the short-range interactions and a point charge, dipole-dipole potential function for the long-range interactions between the four atoms. The method of constructing this surface has been described¹¹ previously for HF(v_1) + HF(v_2) interactions and, therefore, is not repeated here.

The quasi-classical procedure described in Ref. 12 was used to examine the collision dynamics of diatomic-diatom energy-transfer processes. The Hamiltonian equation that describes the four-particle system was written in generalized coordinates, and the resulting set of 18 equations was integrated on a CDC 7600 computer. The initial vibrational states of HF(v_1, J_1) and DF(v_2, J_2) were assigned the vibrational quantum numbers v_1 and v_2 , respectively. Calculations were made with values of v_1 and v_2 varying from 0 through 4. The rotational quantum numbers J_1 and J_2 were Monte-Carlo selected for the calculations involving $v \rightarrow v$ and $v \rightarrow R$ energy-transfer processes. The initial values of the coordinates in each collision were determined by means of (1) a fixed relative-translational energy of the reactants, (2) a chosen initial relative separation between the centers of mass of the diatomic molecules, (3) chosen values of the rotational quantum numbers J_1 and J_2 , (4) the impact parameter, (5) the vibrational phase angles of both molecules, (6) two sets of orientational angles, and (7) the rotational planes of both molecules. Averaging over initial internal states of HF(v_1, J_1) and DF(v_2, J_2) was carried out by the technique described by Porter, Raff, and Miller.¹³ For excited vibrational states, the calculation of the initial values of the momenta P_i ($i = 1, \dots, 9$) is more difficult because the initial amplitudes of both molecules are no longer the classical turning points, and the internal momentum vectors are

no longer perpendicular to the bond axis. For this case, a method based on Euler angles and adequately described in Ref. 12 was used. The distance R between the center of mass of the HF and DF molecules was taken to be 8 a.u. This value is large enough to ensure a negligible initial interaction energy. Relative translational energies were assigned values that ranged from 0.5 to 6 kcal/mole. Approximately 200 trajectories were run for each initial set of parameters. A uniform distribution was used for the square of the impact parameter b . All runs were made with a maximum impact parameter of 2.5 Å. The step size was 5.7×10^{-17} sec. The integration technique, which has not been reported in the literature,^{*} was faster than the Runge-Kutta-Gill procedure,¹⁴ with the accuracy of the integration tested by changes in the step size and by integration backwards along selected trajectories. As an additional verification of numerical accuracy, all trajectories were checked at each point along the trajectory for conservation of total energy and total angular momentum. Computation time for a single trajectory was dependent on the initial parameters but was, on the average, about 9 sec per trajectory on the CDC 7600 computer.

The final properties of each trajectory were analyzed to determine the nature of the collision, i.e., the total angular momentum and vibrational-rotational energy of the HF and DF molecules. The partition of the internal energy between vibrational and rotational energy was determined from the internal energy of the HF and DF molecule and their total angular momentum. The actual technique for calculating the partitioning of the internal energy has been described previously¹⁵ and is not repeated here. The $v \rightarrow v$ energy-transfer cross sections were calculated by Method 2 described in a previous paper by Wilkins.¹⁶ In Method 2, it is assumed that vibrational energy is transferred in every collision and that only one quantum state is accessible in the transfer process. The energy-transfer cross sections and specific rate coefficients were calculated by means of the equations given by Karplus, Porter, and Sharma.¹⁷

^{*}G. Emanuel, personal communication.

III. RESULTS AND DISCUSSION

A. VIBRATIONAL-TO-ROTATIONAL ENERGY TRANSFER

This trajectory calculation indicates that collision complexes are not formed for typical HF-DF or DF-HF collisions. This result is not unexpected inasmuch as the potential energy surface used is identical to that used for HF-HF and DF-DF collisions. Previous trajectory studies^{10, 11} on the HF-HF and DF-DF systems indicated that dimer formation is not required to explain vibrational self-relaxation of HF($v_1 = 1$) or of DF($v_1 = 1$) in the temperature range at and beyond 300 K. This study shows also that $v \rightarrow R$ processes in HF-DF and DF-HF collisions occur by intramolecular energy exchange. The vibrationally excited HF or DF molecule can convert one or more quanta of its vibrational energy into rotational energy. This $v \rightarrow R$ mechanism is responsible for the high rotational states reported by several authors.^{18, 19} Krogh and Pimentel²¹ results indicate that the direct population of high rotational states by chemical pumping reactions can be ruled out. The $v \rightarrow R$ mechanism proposed by Krogh and Pimentel²¹ were observed in this and previous trajectory studies.^{10, 11} The trajectory studies predicted rapid $v \rightarrow R$ deactivations with large ΔJ changes. Specific $v \rightarrow R$ rate coefficients for HF-DF collisions are given in Tables 1 through 3, and for DF-HF collisions in Tables 4 through 6. The qualitative results of these $v \rightarrow R$ processes are as follows:

1. The incident vibrationally excited HF or DF molecule converts one or more quanta of its vibrational energy into rotational energy through an intramolecular $v \rightarrow R$ energy-transfer mechanism. This $v \rightarrow R$ mechanism is responsible for the formation of high rotational states of HF or DF.
2. The energy defects across the reactions for these $v \rightarrow R$ processes have smaller values than would have been

Table 1. Vibrational-to-Rotational Detailed Rate Coefficients for
HF($v_1 = 1, J_1 = 2$) + DF($v_2 = 0$) at $T = 300$ K

v_1	J_1	v_2	J_2	v'_1	J'_1	v'_2	J'_2	ΔE cm $^{-1}$	k_λ^a
1	2	0	J_2	0	17	0	J_2	2017.0	0.7 ± 0.7
1	2	0	J_2	0	16	0	J_2	1357.0	6.3 ± 1.5
1	2	0	J_2	0	15	0	J_2	733.0	4.9 ± 1.8
1	2	0	J_2	0	14	0	J_2	144.0	7.7 ± 2.2
1	2	0	J_2	0	13	0	J_2	-409.0	2.8 ± 1.4
1	2	0	J_2	0	12	0	J_2	-925.0	5.6 ± 1.9
1	2	0	J_2	0	11	0	J_2	-1404.0	3.5 ± 1.5
1	2	0	J_2	0	10	0	J_2	-1844.0	2.8 ± 1.4
1	2	0	J_2	0	9	0	J_2	-2247.0	1.4 ± 1.0

$a_\lambda = (v_1, J_1, v'_1, J'_1, v'_2, J'_2)$. k_λ is the total rate coefficient for $v \rightarrow R$ relaxation in units of 10^{12} cm 3 /(mole-sec). To obtain rate coefficient for $v \rightarrow R$ relaxation of HF($v_1 = 1, J_1 = 2$) by DF($v_2 = 0, J_2$), multiply k_λ by $(2J_2 + 1) \exp[-E(v_2 = 0, J_2)/kT]/Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

Table 2. Vibrational-to-Rotational Detailed Rate Coefficients for
HF($v_1 = 2, J_1 = 2$) + DF($v_2 = 0$) Collisions at $T = 300$ K

v_1	J_1	v_2	J_2	v'_1	J'_1	v'_2	J'_2	ΔE cm $^{-1}$	k_λ^a
2	2	0	J_2	1	16	0	J_2	1328.0	1.8 ± 0.9
2	2	0	J_2	1	15	0	J_2	728.0	4.8 ± 1.4
2	2	0	J_2	1	14	0	J_2	161.0	2.6 ± 1.0
2	2	0	J_2	1	13	0	J_2	-370.0	3.1 ± 1.2
2	2	0	J_2	1	12	0	J_2	-667.0	2.2 ± 1.0
2	2	0	J_2	1	11	0	J_2	-1328.0	1.3 ± 0.7
2	2	0	J_2	1	10	0	J_2	-1752.0	2.2 ± 1.0
2	2	0	J_2	1	9	0	J_2	-2139.0	2.2 ± 1.0
2	2	0	J_2	0	22	0	J_2	2015.0	0.9 ± 0.6
2	2	0	J_2	0	21	0	J_2	1197.0	3.1 ± 1.2
2	2	0	J_2	0	20	0	J_2	406.0	4.8 ± 1.4
2	2	0	J_2	0	19	0	J_2	-352.0	4.0 ± 1.3
2	2	0	J_2	0	18	0	J_2	-1075.0	4.4 ± 1.4
2	2	0	J_2	0	17	0	J_2	-1770.0	2.6 ± 1.0
2	2	0	J_2	0	16	0	J_2	-2427.0	0.4 ± 0.4

$k_\lambda = (v_1, J_1, v_2, v'_1, J'_1, v'_2, J'_2)$. k_λ is the total rate coefficient for $v \rightarrow R$ relaxation in units of 10^{12} cm 3 /(mole-sec). To obtain rate coefficient for $v \rightarrow R$ relaxation of HF($v_1 = 2, J_1 = 2$) by DF($v_2 = 0, J_2$), multiply k_λ by $(2J_2 + 1) \exp[-E(v_2 = 0, J_2)/kT]/Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

Table 3. Vibrational-to-Rotational Detailed Rate Coefficients for
HF($v_1 = 3, J_1 = 2$) + DF($v_2 = 0$) Collisions at $T = 300$ K

v_1	J_1	v_2	J_2	v'_1	J'_1	v'_2	J'_2	ΔE cm ⁻¹	k_λ^a
3	2	0	J_2	2	15	0	J_2	722.0	3.5 ± 1.2
3	2	0	J_2	2	14	0	J_2	178.0	1.3 ± 0.7
3	2	0	J_2	2	13	0	J_2	-333.0	0.9 ± 0.6
3	2	0	J_2	2	12	0	J_2	-811.0	1.3 ± 0.7
3	2	0	J_2	2	11	0	J_2	-1254.0	3.5 ± 1.2
3	2	0	J_2	2	10	0	J_2	-1662.0	2.3 ± 1.0
3	2	0	J_2	2	9	0	J_2	-2035.0	3.5 ± 1.2
3	2	0	J_2	1	21	0	J_2	1195.0	1.3 ± 0.7
3	2	0	J_2	1	20	0	J_2	437.0	3.1 ± 1.2
3	2	0	J_2	1	19	0	J_2	-291.0	3.1 ± 1.2
3	2	0	J_2	1	18	0	J_2	-989.0	2.6 ± 1.0
3	2	0	J_2	1	17	0	J_2	-1655.0	2.6 ± 1.0
3	2	0	J_2	1	16	0	J_2	-2289.0	1.8 ± 0.7
3	2	0	J_2	0	26	0	J_2	1962.0	0.9 ± 0.6
3	2	0	J_2	0	25	0	J_2	1030.0	1.8 ± 0.7
3	2	0	J_2	0	24	0	J_2	125.0	4.0 ± 1.3
3	2	0	J_2	0	23	0	J_2	-752.0	4.0 ± 1.3
3	2	0	J_2	0	22	0	J_2	-1062.0	2.2 ± 1.0
3	2	0	J_2	0	21	0	J_2	-2421.0	2.6 ± 1.0

$a_\lambda = (v_1, J_1, v_2, v'_1, J'_1, v'_2, J'_2)$. k_λ is the total rate coefficient for $v \rightarrow R$ relaxation in units of 10^{12} cm³/(mole-sec). To obtain rate coefficient for $v \rightarrow R$ relaxation of HF($v_1 = 3, J_1 = 2$) by DF($v_2 = 0, J_2$), multiply k_λ by $(2J_2 + 1) \exp[-E(v_2 = 0, J_2)/kT]/Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

Table 4. Vibrational-to-Rotational Detailed Rate Coefficients for
DF($v_1 = 1, J_1 = 3$) + HF($v_2 = 0$) at $T = 300$ K

v_1	J_1	v_2	J_2	v'_1	J'_1	v'_2	J'_2	ΔE cm $^{-1}$	k_λ^a
1	3	0	J_2	0	20	0	J_2	1427.0	1.3 ± 0.7
1	3	0	J_2	0	19	0	J_2	1010.0	4.8 ± 1.4
1	3	0	J_2	0	18	0	J_2	613.0	4.0 ± 1.3
1	3	0	J_2	0	17	0	J_2	236.0	4.8 ± 1.4
1	3	0	J_2	0	16	0	J_2	-122.0	3.1 ± 1.2
1	3	0	J_2	0	15	0	J_2	-460.0	3.1 ± 1.2
1	3	0	J_2	0	14	0	J_2	-788.0	4.0 ± 1.3
1	3	0	J_2	0	13	0	J_2	-1078.0	2.6 ± 1.0
1	3	0	J_2	0	12	0	J_2	-1353.0	3.5 ± 1.2
1	3	0	J_2	0	11	0	J_2	-1610.0	0.4 ± 0.4
1	3	0	J_2	0	10	0	J_2	-1846.0	0.8 ± 0.6
1	3	0	J_2	0	9	0	J_2	-2061.0	0.4 ± 0.4

$a_\lambda = (v_1, J_1, v_2, v'_1, J'_1, v'_2, J'_2)$. k_λ is the total rate coefficient for $v \rightarrow R$ relaxation in units of 10^{12} cm 3 /(mole-sec). To obtain rate coefficient for $v \rightarrow R$ relaxation of DF($v_1 = 1, J_1 = 3$) by HF($v_2 = 0, J_2$), multiply k_λ by $(2J_2 + 1)$ $\exp[-E(v_2 = 0, J_2)/kT]/Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

Table 5. Vibrational-to-Rotational Detailed Rate Coefficients for
DF($v_1 = 2, J_1 = 3$) + HF($v_2 = 0$) Collisions at $T = 300$ K

v_1	J_1	v_2	J_2	v'_1	J'_1	v'_2	J'_2	ΔE cm $^{-1}$	k_λ^a
2	3	0	J_2	1	19	0	J_2	994.0	2.6 ± 1.0
2	3	0	J_2	1	18	0	J_2	608.0	4.8 ± 1.4
2	3	0	J_2	1	17	0	J_2	241.0	1.8 ± 0.9
2	3	0	J_2	1	16	0	J_2	-107.0	2.2 ± 1.0
2	3	0	J_2	1	15	0	J_2	-436.0	2.6 ± 1.0
2	3	0	J_2	1	14	0	J_2	-745.0	2.2 ± 1.0
2	3	0	J_2	1	13	0	J_2	-1035.0	1.3 ± 0.7
2	3	0	J_2	1	12	0	J_2	-1304.0	1.8 ± 0.9
2	3	0	J_2	1	11	0	J_2	-1554.0	0.9 ± 0.6
2	3	0	J_2	0	25	0	J_2	973.0	3.1 ± 1.2
2	3	0	J_2	0	24	0	J_2	465.0	4.0 ± 1.3
2	3	0	J_2	0	23	0	J_2	-25.0	2.2 ± 1.0
2	3	0	J_2	0	22	0	J_2	-497.0	4.8 ± 1.4
2	3	0	J_2	0	21	0	J_2	-950.0	4.4 ± 1.4

$a_\lambda = (v_1, J_1, v_2, v'_1, J'_1, v'_2, J'_2)$. k_λ is the total rate coefficient for $v \rightarrow R$ relaxation in units of 10^{12} cm 3 /(mole-sec). To obtain rate coefficient for $v \rightarrow R$ relaxation of DF($v_1 = 2, J_1$) by HF($v_2 = 0, J_2$), multiply k_λ by $(2J_2 + 1) \exp[-E(v_2 = 0, J_2)/kT]/Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

Table 6. Vibrational-to-Rotational Detailed Rate Coefficients for
DF($v_1 = 3, J_1 = 3$) + HF($v_2 = 0$) Collisions at $T = 300$ K

v_1	J_1	v_2	J_2	v'_1	J'_1	v'_2	J'_2	ΔE cm $^{-1}$	k_λ^a
3	3	0	J_2	2	20	0	J_2	1372.0	0.4 ± 0.4
3	3	0	J_2	2	19	0	J_2	979.0	1.8 ± 0.9
3	3	0	J_2	2	18	0	J_2	603.0	1.3 ± 0.7
3	3	0	J_2	2	17	0	J_2	246.0	2.2 ± 1.0
3	3	0	J_2	2	16	0	J_2	-92.0	0.4 ± 0.4
3	3	0	J_2	2	15	0	J_2	-412.0	0.8 ± 0.6
3	3	0	J_2	2	14	0	J_2	-712.0	0.8 ± 0.6
3	3	0	J_2	2	13	0	J_2	-994.0	2.6 ± 1.0
3	3	0	J_2	2	12	0	J_2	-1256.0	3.1 ± 1.2
3	3	0	J_2	2	11	0	J_2	-1499.0	0.8 ± 0.6
3	3	0	J_2	1	24	0	J_2	476.0	1.3 ± 0.7
3	3	0	J_2	1	23	0	J_2	0.0	2.2 ± 1.0
3	3	0	J_2	1	22	0	J_2	-459.0	2.6 ± 1.0
3	3	0	J_2	1	21	0	J_2	-900.0	2.6 ± 1.0
3	3	0	J_2	1	20	0	J_2	-1323.0	2.2 ± 1.0
3	3	0	J_2	0	30	0	J_2	1044.0	1.3 ± 0.7
3	3	0	J_2	0	29	0	J_2	452.0	3.1 ± 1.2
3	3	0	J_2	0	28	0	J_2	-123.0	2.2 ± 1.0
3	3	0	J_2	0	27	0	J_2	-682.0	4.0 ± 1.3
3	3	0	J_2	0	26	0	J_2	-1224.0	1.8 ± 0.9
3	3	0	J_2	0	25	0	J_2	-1749.0	4.0 ± 1.3

$a_\lambda = (v_1, J_1, v_2, J_2, v'_1, J'_1, v'_2, J'_2)$. k_λ is the total rate coefficient for $v \rightarrow R$ relaxation in units of 10^{12} cm 3 /(mole-sec). To obtain rate coefficient for $v \rightarrow R$ relaxation of DF($v_1 = 3, J_1 = 3$) by HF($v_2 = 0, J_2$), multiply k_λ by $(2J_2 + 1) \exp[-E(v_2 = 0, J_2)/kT]/Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

predicted if both reactant and product species were assumed to be rotationless.

3. Little change occurs in the internal energy state of the target molecule.

Higher rotational states of DF are populated in $DF(v) + HF$ collisions than in $HF(v) + DF$ collisions because the rotational energy of DF at each value of J is slightly higher than one-half that of HF at the same value of J . Since a quantum of vibrational energy of DF is approximately 75% that of HF, the J -states of DF are less than twice those of HF. The net effect indicates only a slight increase in the J -states for DF as compared with those for HF. The results in Tables 1 through 6 indicate that the deuterated species of the hydrogen halides relax more slowly than their hydrogenated analogs.

Detailed rate coefficients $k_{v_1', v_2'; v_1'', v_2''}$ are listed in Tables 7 through 10 for $v \rightarrow R$ deactivation processes that occur in $HF(v_1) + DF(v_2)$ and $DF(v_1) + HF(v_2)$ collisions. The overall rate coefficients k_{vR} in each table increase slightly with increasing v . Rate coefficients are given in Tables 8 and 10 for collisions of vibrationally excited species, i. e., $HF^* + DF^*$ or $DF^* + HF^*$). Within calculated error, $k_{v_1', v_2'; v_1'', v_2''}$ and k_{vR} are almost identical. Analysis of the trajectory results indicates a temperature dependence of $T^{0.5}$ for the $v \rightarrow v$ and $v \rightarrow R$ energy-transfer processes.

The rate coefficients given in Tables 7 through 10 indicate an increase in the number of $v \rightarrow R$ channels. Those in Tables 7 and 9 indicate a decrease in the specific rate coefficients for $v \rightarrow R$ processes with increasing v for collisions involving only vibrationally excited species. The overall rate coefficients presented in Tables 7 and 9 are not comparable to the effective quenching rate coefficients measured in the laboratory. The predicted large increase in the ratio $k_{vR}(v = 2)/k_{vR}(v = 1)$ is due to the increase in $v \rightarrow R$ energy-transfer processes that results from the opening of two channels for conversion of vibrational energy into rotational energy. Kwok and Wilkins⁸ found that the rate coefficients for $v \rightarrow R$ deactivation of $DF(v)$ by HF have a v^2 vibrational dependence. The rate coefficients

Table 7. Rate Coefficients $k_{v_1, v_2; v'_1, v'_2}$ for Vibrational-to-Rotational Energy Transfer in $\text{HF}(v_1) + \text{DF}(v_2)$ Collisions at $T = 300 \text{ K}$

v_{11}	v_2	v'_1	v'_2	$k_{v_1, v_2; v'_1, v'_2}^a$	k_{vR}^a
1	0	0	0	35.7 ± 3.0	35.7 ± 3.0
2	0	1	0	21.1 ± 2.7	
2	0	0	0	20.2 ± 2.7	41.3 ± 3.1
3	0	2	0	16.7 ± 2.4	
3	0	1	0	15.0 ± 2.3	
3	0	0	0	15.4 ± 2.3	47.1 ± 3.1
4	0	3	0	14.5 ± 2.3	
4	0	2	0	11.0 ± 2.1	
4	0	1	0	12.8 ± 2.2	
4	0	0	0	11.4 ± 2.1	49.7 ± 3.1

^aIn units of $10^{12} \text{ cm}^3/(\text{mole-sec})$.

Table 8. Rate Coefficients $k_{v_1, v_2; v'_1, v'_2}$ for Vibrational-to-Rotational Energy Transfer in $\text{HF}(v_1) + \text{DF}(v_2)$ Collisions at $T = 300 \text{ K}$

v_1	v_2	v'_1	v'_2	$k_{v_1, v_2; v'_1, v'_2}$	$k_{v_R}^a$
1	1	1	0	1.7 ± 0.3	
1	1	0	1	2.0 ± 0.3	
1	1	0	0	1.0 ± 0.2	4.7 ± 0.3
1	2	1	1	1.5 ± 0.2	
1	2	1	0	0.9 ± 0.2	
1	2	0	2	1.8 ± 0.3	
1	2	0	1	0.5 ± 0.1	
1	2	0	0	0.7 ± 0.2	5.4 ± 0.4
1	3	1	2	1.3 ± 0.2	
1	3	1	1	1.0 ± 0.2	
1	3	1	0	0.6 ± 0.2	
1	3	0	3	1.5 ± 0.2	
1	3	0	2	0.7 ± 0.2	
1	3	0	1	0.3 ± 0.1	
1	3	0	0	0.5 ± 0.1	5.9 ± 0.3
2	2	2	1	1.4 ± 0.2	
2	2	2	0	0.6 ± 0.2	
2	2	1	2	1.1 ± 0.2	
2	2	1	1	0.4 ± 0.1	
2	2	1	0	0.5 ± 0.1	
2	2	0	2	1.0 ± 0.2	
2	2	0	1	1.3 ± 0.2	
2	2	0	0	0.5 ± 0.1	5.8 ± 0.3

^aIn units of $10^{13} \text{ cm}^3/(\text{mole-sec})$.

Table 9. Rate Coefficients $k_{v_1, v_2; v'_1, v'_2}$ for Vibrational-to-Rotational Energy Transfer in $DF(v_1) + HF(v_2)$ Collisions at $T = 300$ K

v_1	v_2	v'_1	v'_2	$k_{v_1, v_2; v'_1, v'_2}^a$	k_{vR}^a
1	0	0	0	32.8 ± 3.0	32.8 ± 3.0
2	0	1	0	20.2 ± 2.6	
2	0	0	0	18.5 ± 2.6	38.7 ± 3.1
3	0	2	0	14.2 ± 2.3	
3	0	1	0	10.9 ± 1.9	
3	0	0	0	16.4 ± 2.4	41.5 ± 2.9
4	0	3	0	12.3 ± 2.2	
4	0	2	0	11.9 ± 2.2	
4	0	1	0	11.1 ± 2.1	
4	0	0	0	12.3 ± 2.2	47.5 ± 3.1

^aIn units of $10^{12} \text{ cm}^3/(\text{mole-sec})$.

Table 10. Rate Coefficients $k_{v_1, v_2; v'_1, v'_2}$ for Vibrational-to-Rotational Energy Transfer in $DF(v_1) + HF(v_2)$ Collisions at $T = 300$ K

v_1	v_2	v'_1	v'_2	$k_{v_1, v_2, v'_1, v'_2}^a$	$k_{v_R}^a$
1	1	1	0	1.8 ± 0.2	
1	1	0	1	1.9 ± 0.2	
1	1	0	0	0.9 ± 0.2	4.6 ± 0.3
1	2	1	1	1.6 ± 0.2	
1	2	1	0	0.9 ± 0.2	
1	2	0	2	1.6 ± 0.2	
1	2	0	1	0.6 ± 0.2	
1	2	0	0	0.7 ± 0.2	5.4 ± 0.3
1	3	1	2	1.5 ± 0.2	
1	3	1	1	1.0 ± 0.2	
1	3	1	0	0.7 ± 0.2	
1	3	0	3	1.5 ± 0.2	
1	3	0	2	0.6 ± 0.2	
1	3	0	1	0.2 ± 0.1	
1	3	0	0	0.5 ± 0.1	6.0 ± 0.3
2	2	2	1	1.5 ± 0.2	
2	2	2	0	0.7 ± 0.2	
2	2	1	2	1.1 ± 0.2	
2	2	1	1	0.4 ± 0.1	
2	2	1	0	0.5 ± 0.2	
2	2	0	2	1.0 ± 0.2	
2	2	0	1	0.3 ± 0.1	
2	2	0	0	0.5 ± 0.2	6.0 ± 0.3

^aIn units of $10^{13} \text{ cm}^3/(\text{mole-sec})$.

$k_{v_1, v_2; v'_1, v'_2}$ for deactivation from a given initial v_1 level to the final v'_1 level are approximately equal. The results in Tables 7 and 9 imply that the total quenching rate coefficient for $v \rightarrow R$ deactivation should perhaps be partitioned equally among the $(v_1 \rightarrow v'_1)$ transitions possible from a given v level. The measured $v \rightarrow R$ rate coefficients represent total deactivation rates from each initial vibrational level v . The product hydrogen halide molecules are distributed over all the vibrational levels below the initial vibrational level.

B. VIBRATIONAL-TO-VIBRATIONAL ENERGY TRANSFER

Because of the large endothermicity (1055 cm^{-1}) in $\text{DF}(v_1 = 1) + \text{HF}(v_2 = 0)$ collisions, it has been confirmed in laser-excited induced fluorescence experiments that the $v \rightarrow v$ process probably does not occur. The double exponential decay observed in $\text{HF}(v_1 = 1) + \text{DF}(v_2 = 0)$ collisions does not occur in $\text{DF}(v_1 = 1) + \text{HF}(v_2 = 0)$ collisions. Rate coefficients are given in Tables 11 and 12 for room-temperature $v \rightarrow v$ energy-transfer processes obtained from this trajectory study. The collision dynamics indicate quite clearly that, in $v \rightarrow v$ transfer in $\text{HF}(v_1) + \text{DF}(v_2)$ and $\text{DF}(v_1) + \text{HF}(v_2)$ collisions, vibrationally excited HF molecules transfer vibrational energy to the DF molecules. This result concurs with the laser-excited induced fluorescence experiments. The $v \rightarrow v$ process $\text{DF}(v_1 = 1) + \text{HF}(v_2 = 0) \rightarrow \text{DF}(v'_1 = 0) + \text{HF}(v'_2 = 1)$ has a very small cross section because of its large endothermicity (1055 cm^{-1}). As a consequence, trajectory studies were completed only for $v \rightarrow v$ processes that were exothermic. It was not possible to calculate the ΔE energy mismatch for the endothermic and exothermic processes without the appropriate rate coefficient in the endothermic direction for the $v \rightarrow v$ process; thus, column 6 of Tables 11 and 12 is left blank. The energy mismatch calculated under the assumption that both reagent and product HF or DF molecules have zero rotational energy is given in column 7. Previous trajectory studies^{10,11} have shown

Table 11. Rate Coefficients for Vibrational-to-Vibrational Energy Transfer
 $\text{HF}(v_1) + \text{DF}(v_2) \rightarrow \text{HF}(v_1 - 1) + \text{DF}(v_2 + 1)$

v_1	v_2	$v_1 - 1$	$v_2 + 1$	$k_{v_1, v_2; v_1 - 1, v_2 + 1}$ $10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$	$\Delta E,^a$ cm^{-1}	$\Delta E,^b$ cm^{-1}
1	0	0	1	1.6 ± 0.9		-1056.0
2	0	1	1	2.2 ± 1.0		-882.0
3	0	2	1	3.1 ± 1.2		-714.0
4	0	3	1	4.4 ± 1.4		-553.0
1	1	0	2	7.9 ± 1.8		-1147.0
1	2	0	3	3.1 ± 1.2		-1238.0
1	3	0	4	1.3 ± 0.7		-1326.0
2	2	1	3	3.5 ± 1.3		-1064.0

^a ΔE is a function of eight quantum numbers ($v_1, J_1, v_2, J_2, v'_1, J'_1, v'_2, J'_2$).

^b ΔE in this column is defined as a function of vibrational quantum numbers ($v_1, v_2; v'_1, v'_2$).

Table 12. Rate Coefficients for Vibrational-to-Vibrational Energy Transfer
 $DF(v_1) + HF(v_2) \rightarrow DF(v_1 + 1) + HF(v_2 - 1)$

v_1	v_2	$v_1 + 1$	$v_2 - 1$	$k_{v_1, v_2; v_1+1, v_2-1}$ $10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$	ΔE^a cm^{-1}	ΔE^b cm^{-1}
1	1	2	0	10.1 ± 2.0		-1147
1	2	2	1	8.8 ± 1.9		-973
1	3	2	2	7.0 ± 1.7		-805
2	2	3	1	4.8 ± 1.4		-1064

^a ΔE is a function of eight quantum numbers ($v_1, J_1, v_2, J_2; v'_1, J'_1, v'_2, J'_2$).

^b ΔE in this column is defined as a function of vibrational quantum numbers ($v_1, v_2; v'_1, v'_2$).

that, in order to calculate a realistic energy-defect for these processes, one must consider the rotational states of the reagent and product species. This trajectory study indicates also that multiple $v \rightarrow v$ exchange processes do not occur with any great probability. If such processes did occur, we would expect $v \rightarrow v$ exchange from $DF(v = 2)$ to $HF(v = 1)$. No collisions were observed in which the DF molecule transferred vibrational energy to the HF molecule. The rate coefficients for $v \rightarrow v$ processes $HF(v_1) + DF(v_2 = 0) \rightarrow HF(v'_1 = v_1 - 1) + DF(v'_2 = 1)$ with $v_1 = 1$ through 4, respectively, increase with increasing vibrational quantum number v_1 . The computed rate coefficients for the $v \rightarrow v$ processes were $k(v_1 = 1, v_2 = 0; v'_1 = 0, v'_2 = 1) = 1.6 \times 10^{12} \text{ cm}^3/(\text{mole-sec})$ and $k(v_1, v_2 = 0; v'_1 = 0, v'_2 = 1) = 1.4^{(v_1 - 1)} k(1, 0; 0, 1)$ at 300 K. There is an increase in these rate coefficients with decreasing energy-defect.

For $HF(v_1 = 1) + DF(v_2 = 0)$ collisions, the calculated $v \rightarrow v$ room-temperature rate coefficient $k^{vv} = (1.6 \pm 0.9) \times 10^{12} \text{ cm}^3/(\text{mole-sec})$ can be compared with the reported ($v \rightarrow v + v \rightarrow R$) values of $2.5 \times 10^{12} \text{ cm}^3/(\text{mole-sec})$ by Ahl and Cool,³ and Lucht and Cool,⁴ $1.4 \times 10^{12} \text{ cm}^3/(\text{mole-sec})$ by Bott and Cohen,² and $1.2 \times 10^{12} \text{ cm}^3/(\text{mole-sec})$ by Hinchey.¹ It is difficult to assess the actual value of rate coefficient for $v \rightarrow v$ processes because the $v \rightarrow R$ and the $v \rightarrow v$ processes are coupled in the experimental measurement. The measured rate coefficients, therefore, represent the sum of the contributions from the $v \rightarrow v$ and the $v \rightarrow R$ energy-transfer processes. The rate coefficients for the $v \rightarrow v$ processes $HF(v_1 = 1) + DF(v_2) \rightarrow HF(v'_1 = 0) + DF(v'_2 = v_2 + 1)$ with $v_2 = 1$ through 3 decrease with increasing v_2 . These rate coefficients decrease with increasing energy defect. The rate coefficients for $v \rightarrow v$ processes $DF(v_1 = 1) + HF(v_2) \rightarrow DF(v'_1 = 2) + HF(v'_2 = v_2 - 1)$ with $v_1 = 1$ through 3 decrease slightly with increasing v_2 . Since there is an increase in energy defect, we believe that these $v \rightarrow v$ rate coefficients should exhibit an increase with increasing v_2 . The rate coefficients for $v \rightarrow v$ exchange for $HF(v_1 = 1) + DF(v_2 = 1)$ collisions and $DF(v_1 = 1) + HF(v_2 = 1)$ should be identical. The trajectory study predicts a value of $(7.9 \pm 1.8) \times 10^{12} \text{ cm}^3/(\text{mole-sec})$ for $v \rightarrow v$ exchange for

HF($v_1 = 1$) + DF($v_2 = 1$) collisions and a value of $(10.1 \pm 2.0) \times 10^{12} \text{ cm}^3/(\text{mole-sec})$ for DF($v_1 = 1$) + HF($v_2 = 1$) collisions. Both values are within the statistical error. This type of discrepancy might explain why the calculated $v \rightarrow v$ rate coefficients for DF($v_1 = 1$) + HF(v_2) collisions were found not to increase with increasing energy defect. There are no experimental results available with which to compare these rate coefficients for $v \rightarrow v$ energy-transfer processes from the upper vibrational levels. These theoretical results provide insights into the mechanisms of $v \rightarrow v$ energy-transfer processes from upper vibrational levels in hydrogen fluoride and deuterium fluoride systems.

C. VIBRATIONAL RELAXATION OF HF($v_1 = 1$) BY DF($v_2 = 0$)
AND OF DF($v_1 = 1$) BY HF($v_2 = 0$)

The detailed rate coefficients for the $v \rightarrow R$ energy-transfer processes listed in Tables 1 and 4 together with the $R \rightarrow (R', T)$ rate coefficients presented in recent papers by Wilkins^{10,11} were used in a rotational nonequilibrium model to calculate temperature-dependent quenching rate coefficients for vibrational relaxation of HF($v_1 = 1$) by DF($v_2 = 0$) and of DF($v_1 = 1$) by HF($v_2 = 0$). A description of this rotational nonequilibrium model was discussed previously by Wilkins and Kwok* and will not be repeated here.

In Figs. 1 and 2, the results are seen to be in good agreement with measured relaxation rates. Blauer et al.²² reported that, within their experimental scatter, the vibrational relaxation times of these two systems are identical in the temperature range between 1500 and 4000 K. The calculated results obtained from the rotational nonequilibrium model tend to approach those of Blauer et al.²² The relaxation times for DF($v_1 = 1$) by HF($v_2 = 0$) lie between those for DF($v_1 = 1$) by DF($v_2 = 0$) and HF($v_1 = 1$) by HF($v_2 = 0$). P_T is larger for DF($v_1 = 1$) + DF($v_2 = 0$) collisions than for

* R. L. Wilkins and M. A. Kwok, "Temperature Dependence of HF($v_1 = 1$) + HF($v_2 = 0$) Vibrational Relaxation," TR-0078(3603)-5, The Aerospace Corp., to be published.

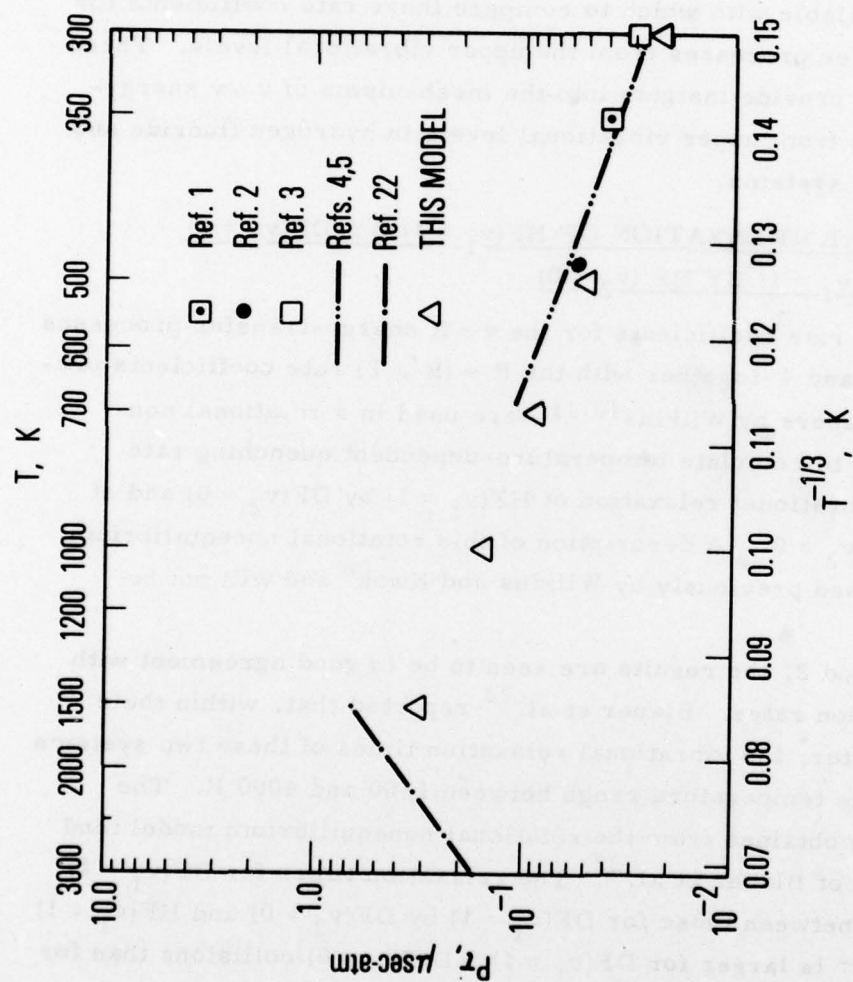


Fig. 1. Vibrational Relaxation of HF($v_1 = 0$) by DF($v_2 = 0$).
P vs T and $T^{-1/3}$

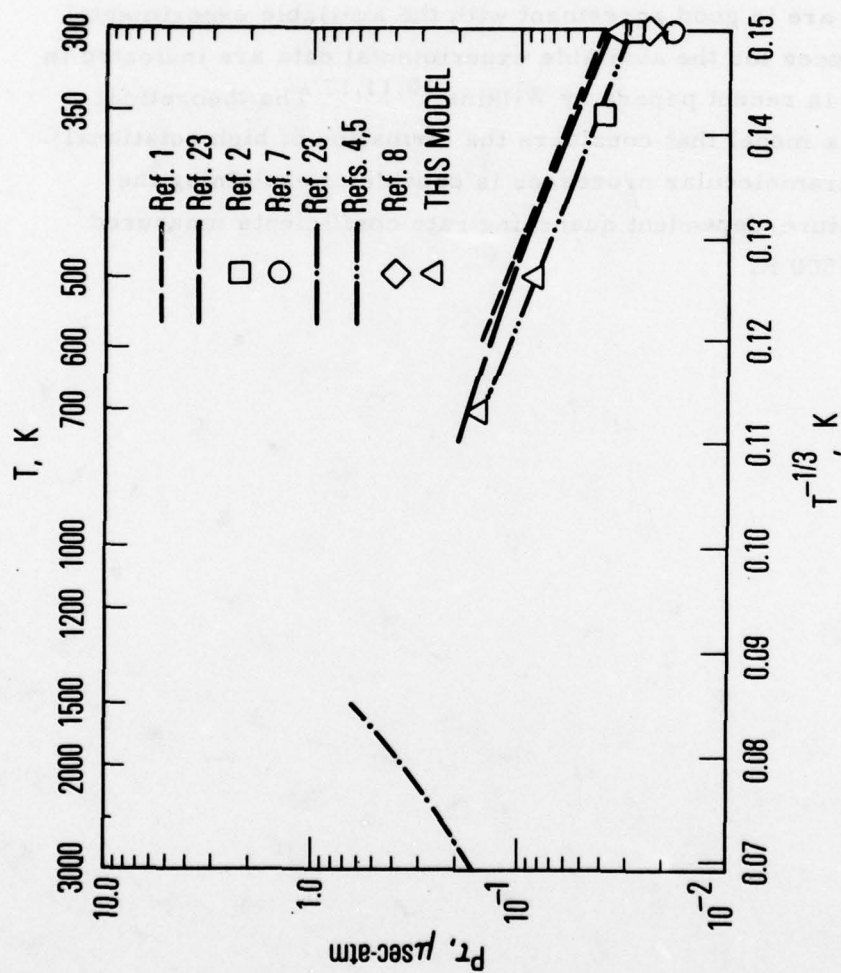


Fig. 2. Vibrational Relaxation of $\text{DF}(v_1 = 1)$ by $\text{HF}(v_2 = 0)$.
P vs T and $T^{-1/3}$

$\text{HF}(v_1 = 1) + \text{HF}(v_2 = 0)$ collisions. The $v \rightarrow R$ transfer in $\text{HF}(v_1 = 1) + \text{HF}(v_2 = 0)$ collisions occurs more rapidly than in $\text{DF}(v_1 = 1) + \text{DF}(v_2 = 0)$ collisions. The relaxation times for $\text{HF}(v_1 = 1)$ by $\text{DF}(v_2 = 0)$ lie below those of $\text{HF}(v_1 = 1)$ by $\text{HF}(v_2 = 0)$. The values of the ratios $k_{\text{HF-HF}}/k_{\text{DF-DF}}$, $k_{\text{DF-HF}}/k_{\text{HF-DF}}$, and $k_{\text{HF-HF}}/k_{\text{HF-DF}}$ obtained from the theoretical model are in good agreement with the available experimental data. The references for the available experimental data are indicated in Figs. 1 and 2 and in recent papers by Wilkins.^{10,11,17} The theoretical results show that a model that considers the formation of high rotational states by $v \rightarrow R$ intramolecular processes is capable of explaining the observed temperature-dependent quenching rate coefficients measured between 300 and 1500 K.

IV. CONCLUSIONS

This trajectory study predicts that, in $\text{HF}(v_1) + \text{DF}(v_2)$ and $\text{DF}(v_1) + \text{HF}(v_2)$ collisions, $v \rightarrow v$ processes occur by intermolecular energy exchange with single-quantum v transitions. The vibrationally excited HF species transfer vibrational energy to the DF species. The vibrationally excited DF species do not transfer vibrational energy to the HF species. The rate coefficients for the $v \rightarrow v$ processes $\text{HF}(v_1) + \text{DF}(v_2 = 0) \rightarrow \text{HF}(v'_1 = v_1 - 1) + \text{DF}(v'_2 = 1)$ with $v_1 = 1$ through 4, respectively, increase with increasing vibrational quantum number v_1 . The rate coefficients for the $v \rightarrow v$ processes $\text{HF}(v_1 = 1) + \text{DF}(v_2) \rightarrow \text{HF}(v'_1 = 0) + \text{DF}(v'_2 = v_2 + 1)$ with $v_2 = 1$ through 3 decrease with increasing v_1 . In the $v \rightarrow R$ processes, which are nonresonant energy-transfer processes, several quanta of vibrational energy of $\text{HF}(v_1)$ or $\text{DF}(v_1)$ are converted into rotational energy of the molecule. The $v \rightarrow R$ processes occur by intramolecular energy-transfer mechanisms with multiple-quanta v transitions. This study predicts that $v \rightarrow v$ up-pumping coupled with $v \rightarrow R$ deactivation with large ΔJ changes provide the mechanisms to produce high J states in HF and DF chemical lasers. This study predicts that collision complexes are not formed for typical HF + DF or DF + HF collisions at 300 K and beyond. A rotational nonequilibrium model is used to calculate temperature-dependent quenching rate coefficients for vibrational relaxation of $\text{HF}(v_1 = 1)$ by $\text{DF}(v_2 = 0)$ and of $\text{DF}(v_1 = 1)$ by $\text{HF}(v_2 = 0)$. The results were found to be in good agreement with available experimental data.

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